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Synthesis and Polymerization Reactions of Cyclic Imino Ethers. VI. Polymers with Biphenyl Structure

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ABSTRACT: A monomer of the AB-type and a bifunctional comonomer of the AA-type containing two 2-oxazoline rings and a biphenyl structural unit were prepared from the corresponding carboxylic acids via their esterification and subsequent amidation with an aminoalcohol. The cyclization of an amide to 2-oxazoline structure was achieved by treatment with thionyl chloride followed by liberation of the free base with sodium hydrocarbonate in an aqueous solution. The prepared monomers were used for the polyaddition polymerization of the AB-type monomer having a 2-oxazoline and phenol group bound on adjacent rings of the biphenyl structure in solution. The monomer of the AA-type was used for AA+BB-type polyaddition reactions with aliphatic dicarboxylic acids. Both types of polymerizations have been performed in melt and in solution. The structures of the polymers were determined, and the thermal properties of the polymers were evaluated. Liquid-crystalline (LC) structures of the prepared polymers were observed by DSC measurements and optical microscopy. The polyaddition reactions of the monomers containing a 2-oxazoline ring and a biphenyl unit represent a new efficient way for the preparation of a biphenyl unit containing poly(ether amide)s and poly(ester amide)s. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 000: 000–000, 2012

KEYWORDS: 2-oxazolines; addition polymerization; biphenyl; high-temperature materials; liquid-crystalline polymers (LCP); poly (ester amide)s; step-growth polymerization

INTRODUCTION Cyclic imino ethers, mainly 2-oxazolines, are versatile compounds with broad utilization in organic and polymer chemistry.[1] 2-Oxazolines react with carboxylic acids,[2] phenols,[3] and thiols.[3] They also take part in cationic ring opening polymerizations and enzymatic ring-opening polyaddition reactions.[4,5] It is noteworthy to mention that the 2-oxazoline ring behaves as a bifunctional group in cationic polymerizations and as a monofunctional moiety in addition reactions.

In previous articles,[6–11] we have shown broad perspectives of the polymerization of 2-oxazoline containing compounds either in the AA+BB, or in the AB and AB_2 modes, as well as in cationic (co)polymerization, where a number of different polymers of the poly(ether amide), poly(ester amide), poly (amino amide), or poly(imino ether) types were formed.[4] These reactions proceed due to the presence and reactions of different functional groups on the basic skeleton of the molecule of the monomer. In such a way, poly(ester amide)s with a broad range of melting temperatures have been synthesized in AA+BB mode from the same bis-2-oxazoline as the AA compounds and with dicarboxylic acids as the BB monomer with various length aliphatic linkers between acid groups.[9] However, there exists another way to enhance the possibilities of the exploitation of such systems, for instance, changing the basic skeleton of the monomer with groups bearing a specific characteristic and/or special property. Recently, we presented the preparation of poly(ether amide)s containing a naphthalene group.[11]

Another example of such a group is a biphenyl structure considered as a mesogen that is typically used for the preparation of liquid crystalline (LC) compounds and LC polymers.[12–18] LC polymers can contain the biphenyl structure incorporated into the main chain or into the side chain. Recently, poly(ester amide)s containing a biphenyl moiety in the main chain were prepared from butyrolactone, different aliphatic or aromatic diamines, and dichlorides of dicarboxylic acids.[19]

In our studies on the synthesis and polymerization of 2-oxazolines, we prepared polymers containing a mesogen group in the molecule where the biphenyl unit was chosen as the mesogen. Two different compounds, 4-hydroxy-4′-(2-oxazolin-2-yl)biphenyl (**HBiOX**) and 4,4′-bis (2-oxazolin-2-yl)

TABLE 1 Conditions and Results of Polyadditions of 4,4′-Bis(2-oxazolin-2-yl)biphenyl (**BiBOX**) with Different Dicarboxylic Acids

No.	Diacid	Amount (mmol)	Solvent (mL)	Temp. (°C)	Time (h)	Yield (%)	M_n (VPO)	T_m (°C)	Note
1	Sebacic	0.5	–	155	5	90	–	270–273	Acid did not dissolved **BiBOX**
2	Sebacic	0.5	DMF/0.3	170	5	95	–		Phase separation
3	Sebacic	0.5	TMS/0.5	180	5	97	–		
4	Sebacic	0.5	DMSO/0.5	180	5	100			
5	Suberic	0.5	TMS/1	180	5	95	8,330	275–292	
6	Adipic	0.5	TMS/1	180	5	100	22,000	303–306	
7	Dodecanedioic	0.5	TMS/1	180	5	95		258–265	
8	Succinic	0.5	TMS/0.5	155	8	91		300–307	

biphenyl (**BiBOX**), were prepared as monomers of AB- and AA–BB-types for polyaddition reactions.

EXPERIMENTAL

Materials

The starting materials including 4′-hydroxy-4-biphenylcarboxylic acid (**HBiAc**) and 4,4′-biphenyldicarboxylic acid (**BiDAc**) were purchased from Aldrich. All other available reagents (Aldrich) were used as received. All solvents used for polymerizations and subsequent measurements were distilled and dried over molecular sieves before the use.

Synthesis of 4′-Hydroxy-4-(2-oxazolin-2-yl) biphenyl (HBiOX)

The ester **(HBiEs)** was prepared from 4′-hydroxy-4-biphenylcarboxylic acid (**HBiAc**) (5 g, 0.023 mol) by heating under reflux in methanol (50 mL) in the presence of a catalytic amount of sulfuric acid (0.11 mL, 0.002 mol) for 5 hours. The reaction yield was 97%. mp 226–229°C. ^{1}H NMR (DMSO-d_6): 3,86 (s, OCH3, 3H), 6,88 (d, ar, 2H), 7,59 (d, ar, 2H), 7,74 (d, ar, 2H), 7,98 (d, ar, 2H), 9,74 (s, Ar-OH, 1H).

The hydroxyamide **HBiAm** was prepared by the reaction of **HBiEs** (2.97 g, 0.013 mol) with 2-aminoethanol (6.35 g, 0.104 mol) at 150°C for 3 hours. The excess of 2-aminoethanol was removed with suction and the residue was poured into water. A white crystalline compound was obtained. The yield: 98%. mp 240–242°C. ^{1}H NMR (DMSO-d_6): 3,35 (q, CH_2N, 2H), 3,52 (d, CH_2O, 2H), 4,75 (s, R—OH, 1H), 6,86 (d, ar, 2H), 7,57 (d, ar, 2H), 7,67 (d, ar, 2H), 7,91 (d, ar, 2H), 8,44 (t, NH, 1H), 9,57 (broad s, Ar—OH, 1H).

HBiOX was prepared by cyclization of **HBiAm** (3.01 g, 0.012 mol) in dichloromethane (70 mL). Thionyl chloride (4.4 mL, 0.06 mol) was added dropwise in an ice bath, and the reaction mixture was stirred for 20 hours at an ambient temperature. The white solid of hydrochloride was isolated, dried, and neutralized with saturated aqueous $NaHCO_3$. A white precipitate was isolated and recrystallized from ethanol. Yield: 79%. mp 238–240°C. ^{1}H NMR (DMSO-d_6): 3,97 (t, CH_2N, 2H), 4,41 (t, CH_2O, 2H), 6,89 (d, ar, 2H), 7,58 (d, ar, 2H), 7,79 (d, ar, 2H), 7,91 (d, ar, 2H), 9,67 (broad s, Ar—OH, 1H), UV (CH_3OH): 220 nm (log $\varepsilon = 4,17$), 297 (log $\varepsilon = 4,38$).

Synthesis of 4,4′-Bis(2-oxazolin-2-yl)biphenyl (BiBOX)

4,4′-Biphenyldicarboxylic acid (***BiDAc***, 4.84 g, 0.02 mol) and thionyl chloride (7.3 mL, 0.1 mol) were heated under reflux for 3 hours. The excess $SOCl_2$ was removed and colorless crystals of biphenyl-4,4′-dicarbonylchloride (**BiDCl**) were obtained. Yield: $\sim$100%. mp = 186–188°C.

BiDCl (5.6 g, 0.02 mol) and 2-chloroethylamine hydrochloride (4.64 g, 0.04 mol) were dispersed in a mixture of aqueous NaOH (4.5 g, 0.08 mol) and dichloromethane (70 mL). A white precipitate was formed immediately. The solid was then separated, washed with water, and dried. A white powder of *N, N′*-Bis(2-chloroethyl)biphenyl-4,4′-dicarboxamide (BiDAm) was obtained. Yield: 99.5%. mp $>$300°C.

BiDAm (5.48 g, 0.015 mol) was dissolved in methanolic KOH (0.03 mol), and the solution was heated under reflux for 3 hours. After cooling, the precipitate was separated and the residue was concentrated. A white solid of **BiBOX** was obtained. Yield: 87%. mp = 320°C, sublimation at 250°C. ^{1}H NMR (DMSO-d_6): 3.99 (t, CH_2N, 4H), 4.43 (t, CH_2O, 4H), 7.83 (d, ar, 4H), 7.97 (d, ar, 4H).

Polymerization in Melt

Calculated amounts of comonomers were weighed in a dry ampoule, which was evacuated and filled with argon several times before sealing. The tube was then immersed in a preheated oil bath. After finishing polymerization, the ampoule was opened; the polymer was dissolved in hot DMF, precipitated in nonsolvent, separated, washed, and dried under vacuum. Detailed polymerization conditions and results are listed in Table 1.

Polymerization in Solution

Calculated amounts of comonomers were weighed in a dry ampoule, solvent was added, and the mixture was bubbled with argon for 5 min and then sealed. The ampoule was immersed in an oil bath preheated to the desired temperature and withdrawn after the desired time. The liquid or viscous product was precipitated in a nonsolvent (methanol, water). The solid product was dissolved in the solvent used during polymerization and precipitated in nonsolvent. Detailed polymerization conditions and results are listed in Table 1.

Analytical Measurements

^{1}H and ^{13}C NMR spectra were measured on an AMX-300 spectrometer (Bruker) operating at 300.13 MHz for ^{1}H and 75.47 MHz for ^{13}C and on a DRX-500 NMR spectrometer (Bruker) operating at 500.13 MHz for ^{1}H and 125.77 MHz for ^{13}C. The samples were measured in DMSO-d$_6$ at room temperature. The solvent was used as a lock and internal standard (δ (^{1}H) = 2.50 ppm, δ (^{13}C) = 39.6 ppm). FTIR spectra were recorded with IR spectrophotometer NICOLET 8700^{TM} (Nicolet, USA) with 64 scans and steps of 4 cm^{-1} in KBr pellets. UV spectra were taken with Shimadzu UV C1650. Melting points were measured on a Koffler melting point apparatus (VEB Analytik, Germany) and are uncorrected.

HPLC measurements were done on a HPLC Agilent 1200 series system equipped with an isocratic pump and UV detection. Measurements were done in a mixture of methanol–water (8/2), at a flow rate of 0.5 mL/min, a C-18 column (Zorbax), and UV-detection at 254 nm.

A number of average molecular weights were measured by vapor pressure osmometry (Knauer, DMSO, 90°C). Thermal analysis was done with a Mettler Toledo DSC instrument at a heating rate of 10 K/min.

The texture of the sample and phase transition temperatures of polymers were determined by a polarizing optical microscope (Nikon Eclipse 80i, cross polarizers) equipped with a heating stage Linkam LTS350) at a heating rate of 10 K/min.

RESULTS AND DISCUSSION

Monomer Synthesis

Two different monomers containing at least one 2-oxazoline structural unit and a biphenyl structure, namely 4-hydroxy-4′-(2-oxazolin-2-yl)biphenyl **(HBiOX)** and 4,4′-bis(2-oxazolin-2-yl)biphenyl (**BiBOX**), were prepared as monomers of the AB- and AA+BB types for polyaddition reactions.

The synthetic approach to the **HBiOX** is shown in Scheme 1. The starting point was an aromatic hydroxy acid **HBiAc**, which was esterified under acid catalysis to an ester **HBiEs**. The treatment of **HBiEs** with ethanolamine for 3 hours at 150°C yielded a hydroxyamide intermediate **HBiAm** which was isolated in high yield (nearly 100%). The cyclization of **HBiAm** with an excess of thionyl chloride was performed by the addition of the reagent to the substrate under cooling with ice bath and then by the agitation of the reaction mixture at room temperature overnight. The desired **HBiOX** was obtained in the hydrochloride form as a white powder. The liberated base was obtained after treatment with potassium hydrogen carbonate in high yield. ^{1}H NMR spectrum (Fig. 1) confirmed the expected structure of the monomer. The reactivity of the hydroxyl group, expressed by the chemical shift δ, equals to 9.67 ppm and is similar to the 2-(4-hydroxyphenyl)-2-oxazoline with δ of the hydroxyl group proton equal to 10.08 ppm described in the first part of this series.[5] The slightly lower value is due to the donor character of the biphenyl structure. However, this value is more than 1 ppm higher than the value of OH groups in hydroquinone, which supports the push-pull effect of phenolic and 2-oxazoline groups connected by a conjugated system. This implies that monomers of the AB-type containing a 2-oxazoline ring and a phenolic group in one molecule will be more reactive compared with the case of the reaction between the appropriate bis(2-oxazoline) and hydroquinone (Scheme 1).

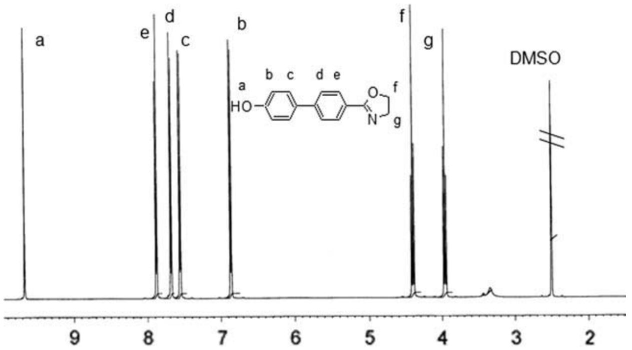


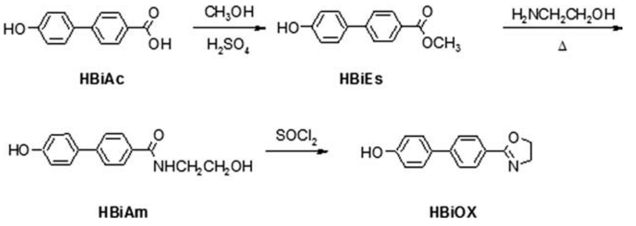
FIGURE 1 ^{1}H NMR spectrum of the 4-hydroxy-4′-(2-oxazolin-2-yl)biphenyl (HBiOX) in DMSO-d$_6$.

The second monomer, containing two 2-oxazoline groups on the biphenyl unit, 4,4′-bis(2-oxazolin-2-yl)biphenyl (**BiBOX**), was prepared from biphenyl-4,4′-(dicarboxylic acid) according to Scheme 2.

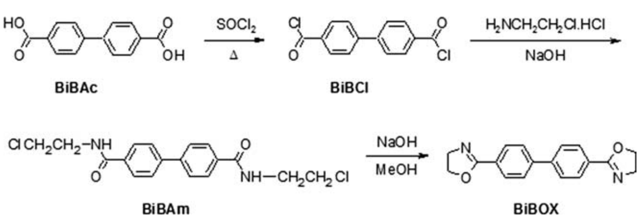
In the first step dichloride of dicarboxylic acid (BiDCl) was prepared by heating the acid (BiDAc) in excess thionyl chloride. The acid chloride provides a bis-chloroethylamide after reacting it with 2-chloroethylamide which, after boiling in KOH/MeOH, provided **BiBOX**. It is noteworthy to mention that a very high reaction yield was obtained in all steps.

AB-Type Polyadditions

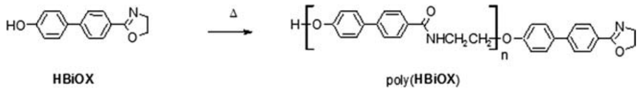
The prepared **HBiOX** was used in thermally initiated polymerization in bulk and in a solution. The treatment of **HBiOX** at a temperature of 245°C, which is slightly higher



SCHEME 1 Synthesis of 4′-hydroxy-4-(2-oxazolin-2-yl)biphenyl (HBiOX).



SCHEME 2 Synthesis of 4,4′-bis (2-oxazolin-2-yl)biphenyl (BiBOX).



SCHEME 3 Polyaddition reaction of 4′-hydroxy-4-(2-oxazolin-2-yl)biphenyl (HBiOX).

than the melting point of the monomer, ensured the homogeneity of the system during polymerization. The duration of the polymerization was 1 hour. Under these conditions, the poly(**HBiOX**) was obtained in 88% yield.

For polymerization in solution, *N*-methylcaprolactam was used as a solvent. However, despite having a very high solvent power, a stepwise precipitation of the polymer from the solution during polymerization was observed. Therefore, short chains were obtained with the degree of polymerization equal to 4, as estimated from NMR. This implies that the melt polyaddition is the only effective way for **HBiOX** polymerization.

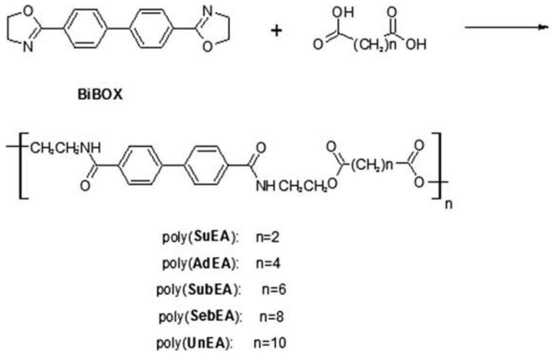
As expected from previous results,[6,20] in the case of polymerization of an AB-type monomer with 2-oxazoline and phenolic functional groups, poly(ether-amide) was formed in the absence of side reactions (Scheme 3). Also in this case, the molar ratio of both the 2-oxazoline and phenol remains the same and is equal to one.

We can see in Figure 2 that the structure of the polymer poly(**HBiOX**) confirmed the following changes in the spectrum. The protons of the oxazoline structure with δ 3.97 and 4.41 ppm are substituted with protons of the opened structure with the chemical shift 4.25 and 4.56 ppm, respectively. The spectrum also shows protons of the 2-oxazoline end groups at δ 5.15 and 4.65 ppm. The ratio of integrals of the chemical shift hydrogen atoms of the linear and end hydrogen atoms determined the average degree of polymerization (DP). In this case, the value is 15. Also, it is evident that the phenolic proton completely disappeared. The values of the chemical shift of aromatic protons and ring protons are slightly shifted to a lower field, which may also be due to the solvent.

AA+BB-Type Polyadditions

The bifunctional monomer **BiBOX** was used in the polymerization of AA+BB-type with aliphatic dicarboxylic acids of different alkylene chain lengths (from succinic to dodecanedioic acids) (Scheme 4). In contrast with the AB polymerizations, phenolic groups as B groups have been replaced by carboxylic groups. This is mainly attributed to the aliphatic OH groups not being reactive enough to provide an addition reaction with the 2-oxazoline ring. Moreover, the push-pull system of the electron-donor phenolic group and the electron-acceptor 2-oxazoline ring of AB-type monomer is necessary for enhancing the reactivity of both groups in the addition reactions. The thermally induced polyaddition of biphenyldicarboxylic acid with 1,3- and 1,4-phenylenebis (2-oxazoline) is an example of a polymerization of aromatic comonomers and has been published previously.[10] All polymerizations were thermally initiated and were attempted to be prepared in a melt or in a solution of high boiling solvents. Conditions and results of all polymerizations are summarized in Table 1. The influence of polymerization conditions during the course of polymerization was studied in the polyaddition of **BiBOX** with sebacic acid. The melt polyaddition of these two comonomers was limited by the very low solubility of **BiBOX** in the melt of sebacic acid. Therefore, polymerization proceeded in a heterogeneous polymerization mixture. For solution polymerization, two high boiling solvents were used: *N, N*-dimethylformamide (DMF) and tetramethylene sulfone (TMS). During polymerization of **BiBOX** with sebacic acid in DMS, phase separation was observed. Therefore, TMS was used in all solution polymerizations. All polyadditions proceeded in high yields (90–100%). The measurement of molecular characteristics of the resultant polymers was complicated by limited solubility in common solvents. As seen in Table 1, only polymers prepared from adipic and suberic acids were soluble in DMSO, and their number average molar masses (M_n) were measured by vapor phase osmometry (VPO). Values of M_n were equal to 22,000 g/mol and 8330 g/mol, which represent 50 and 18 biphenyl units, respectively.

The structure of all polymers prepared by the AA+BB-type polyaddition was confirmed by ^{1}H NMR spectra measured in DMSO-d$_6$ (Fig. 3). In all spectra, signals of the symmetrical biphenyl unit, amidic proton, and ethylene groups take place at almost the same chemical shift. Two doublets at 7.79 and 8.02 ppm can be assigned to protons of the biphenyl unit, while broad peaks at 8.43 ppm represent the proton of the



SCHEME 4 Polyaddition reactions of 4,4′-bis (2-oxazolin-2-yl) biphenyl (BiBOX) with various aliphatic dicarboxylic acids.

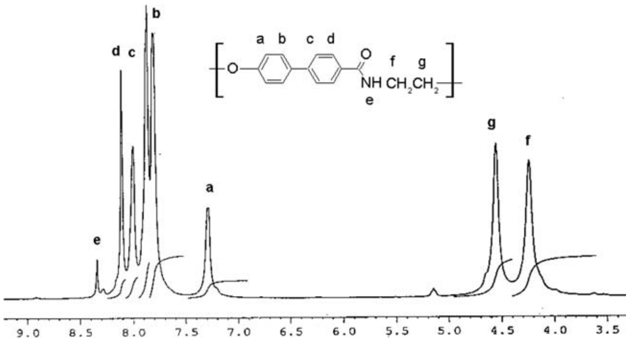


FIGURE 2 ^{1}H NMR spectrum of poly(HBiOX) in D_2SO_4.

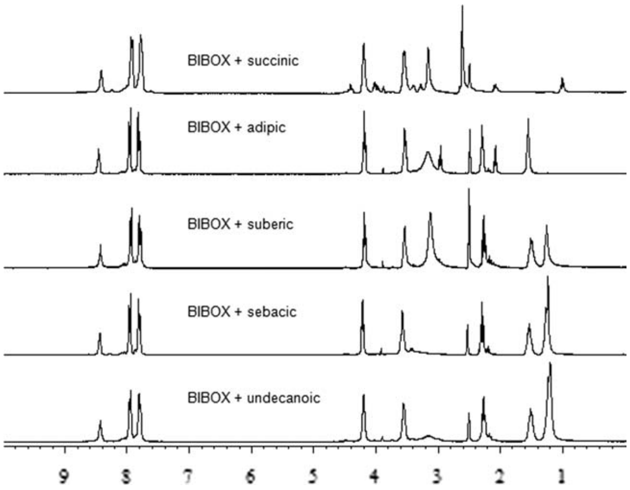


FIGURE 3 ^{1}H NMHR spectra of polymers prepared by polyaddition of BiBOX with various dicarboxylic acids measured in DMSO-d$_6$.

amidic NH group. Peaks at 4.20 and 3.60 ppm can be assigned to the protons of CH_2O and CH_2N, respectively. The others represent signals from alkyl chains. The 2-oxazoline end-groups are present at 4.50 and 4.05 ppm for CH_2O and CH_2N, respectively. The ratio of integrals of ethylene amide protons signals to signals of the end-groups can give information about the degree of polymerization. Although it was not possible to calculate the degree of polymerization (DP) from NMR spectra, it is clearly seen in Figure 3 that the higher DP have polymers prepared from adipic, suberic, and sebacic acids.

IR spectra supported the formation of the ester-amide structure of all polymers (Fig. 4). The C=N bond stretch in an oxazoline unit at 1648 cm^{-1} was substituted in all cases by signals from the C=O stretch of the amidic group at 1641 cm^{-1}. The peaks at 1536 cm^{-1} are characteristic of the C—NH stretch of a secondary amide group, and the signals at 3300–3400 cm^{-1} can be assigned to N—H stretching. These signals are in all cases accompanied with a shoulder at wave numbers higher than 3500 cm^{-1}. All spectra contain signals from an ester group: C=O stretching at 1735 cm^{-1} and signal of C—O stretching at 1287 cm^{-1}. Ring bonds represent signals at 1610, 1491, 845, and 756 cm^{-1}. The last two bands are in the fingerprint region and are characteristic for p-disubstituted benzene rings (Fig. 4).

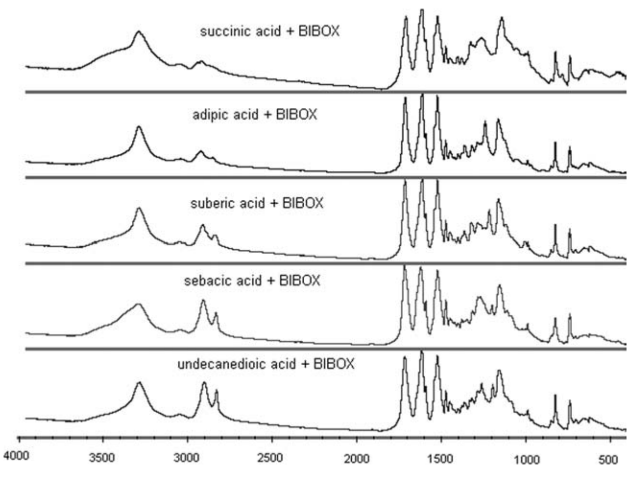


FIGURE 4 IR spectra of polymers prepared in AA+BB mode measured in KBr pellets.

While the area from 500 to 2000 cm^{-1} is almost the same, the area from 2800 to 3500 cm^{-1} depends on the length of aliphatic spacer in the aliphatic part of structural unit. Three small and broad peaks take place in the spectra of the poly (**BiBOX**-succinic acid) at 2963, 2938, and 2875 cm^{-1}. The intensity of all of the peaks increases with increasing the aliphatic chain length; in addition, a shift of all three bands is observed (Fig. 5).

Thermal Properties

Thermal properties of the poly(**HBiOX**) are shown in the Figure 6 where first and second heating scans in thermal intervals between 0 and 300°C are presented. In the first scan, several endotherms are visible at 100, 180, 235, and 293°C. These peaks do not appear in the second scan and probably belong to unstable crystalline areas formed during cooling of the amide bonds formed in the polymerization process.

Another interpretation is based on the phase transitions of the liquid crystalline (LC) phase in the polymer.[11–17] It seems that there is a coincidence between the third endotherm at 235°C and the polymerization temperature at 245°C in bulk polymerization (mp = 238–240°C). A clear movement of the heated monomer was observed at this temperature by means of a microscope during melting point measurements. In fact, the appearance of an LC phase was expected on the basis of previous results, and it was a reason for the synthesis and polymerization of this compound.

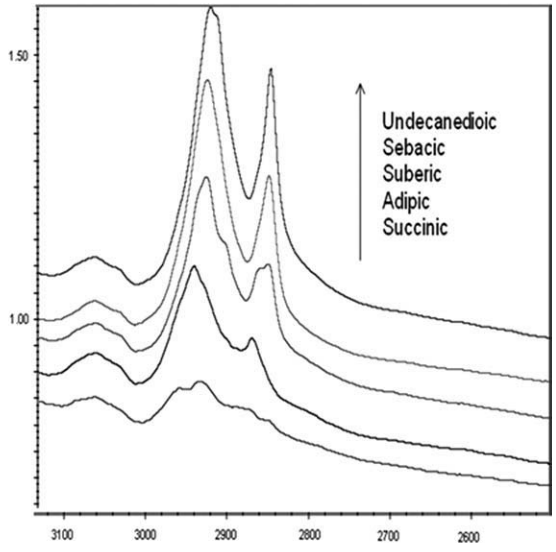


FIGURE 5 Detail of IR spectra of AA+BB polymers of the area from 2500 to 3100 cm^{-1}.

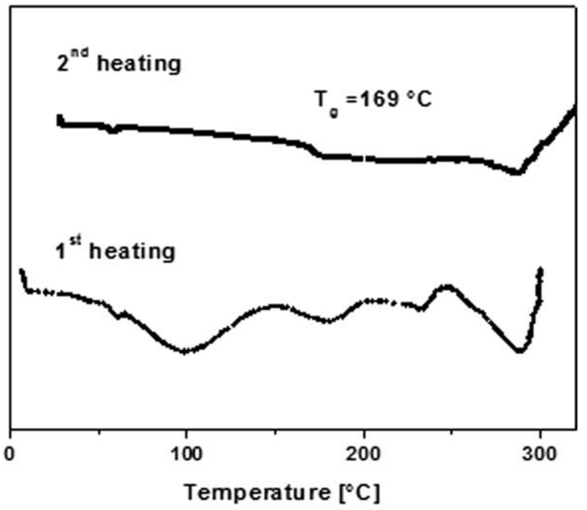


FIGURE 6 Record of first and second heating of poly(HBiOX).

A glassy transition temperature (T_g) of the poly(**HBiOX**) was observed as high as 169°C. This value is higher than T_g of analogous polymers of AB-type containing a phenyl ring, namely poly[2-(4-hydroxyphenyl)-2-oxazoline] with T_g equal to 150°C. As expected, the substitution of the phenyl ring by a biphenyl group increases the stiffness of the polymer chain which causes an increase of T_g of the biphenyl unit containing polymer. In previous articles dedicated to the preparation of naphthalene ring containing poly(ether amides) and poly(ester amides), the glass-transition temperature of poly[2-(6-hydroxy-2-naphthalene-2-yl)-2-oxazoline] prepared by AB-type polyaddition is 182°C, which is higher than the value of AA+BB-type polymers.[11] This corresponds to the larger content of hard aromatic segments in latter type of polymers. The presence of an aliphatic chain should decrease the T_g of the AA+BB-type poly(ester amides). However, the values of T_g in DSC records of all AA+BB were not measurable [Fig. 7(b)]. This may be due to decomposition at higher temperatures during the first heating [broad exotherms, Fig. 7(a)]. Figure 7(a) shows that DSC records of poly(**BiBOX**-succinic acid) and poly(**BiBOX**-adipic acid) contain one endothermic peak assigned to the isotropization process while DSC records of polymers with longer alkyl chain contain two

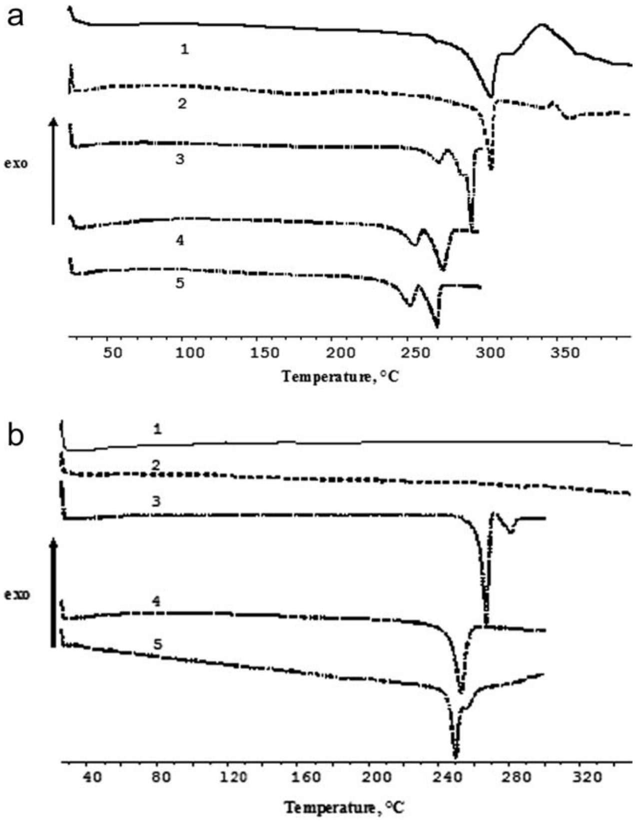


FIGURE 7 Records of the first (a) and second (b) heating of DSC in the temperature range between 25 to 350°C for polymers prepared in AA+BB mode. Used diacid (1) succinic acid (2) adipic acid (3) suberic acid (4) sebacic acid (5) dodecanoic acid.

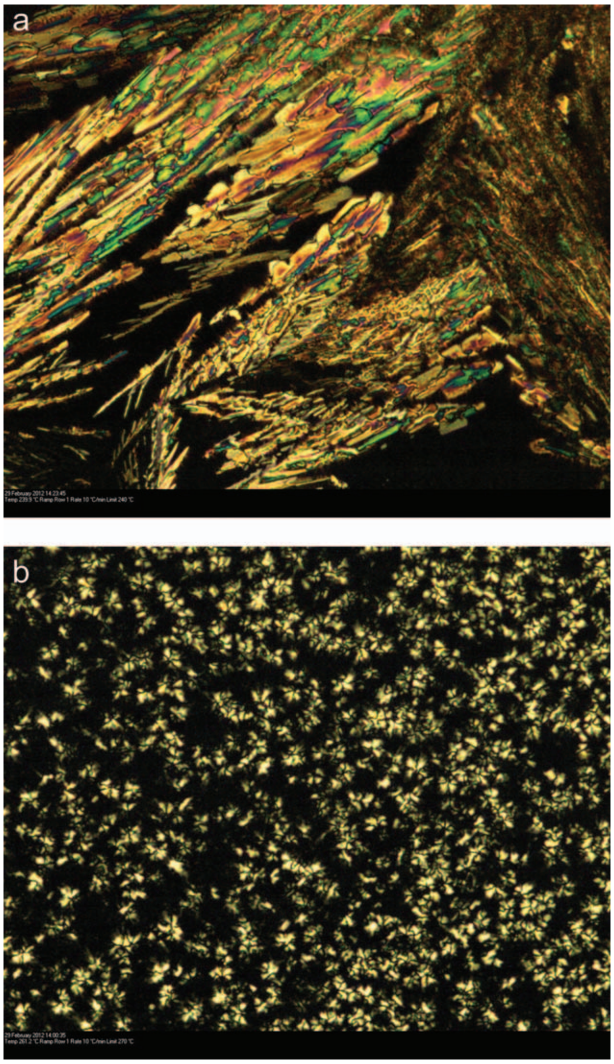


FIGURE 8 Optical microphotographs of BiBOX at 250°C (a) and poly(BiBOX-dodecanedioic acid) at 260°C (b). Width of pictures is 400 μm, and the magnification of an objective is ×20.

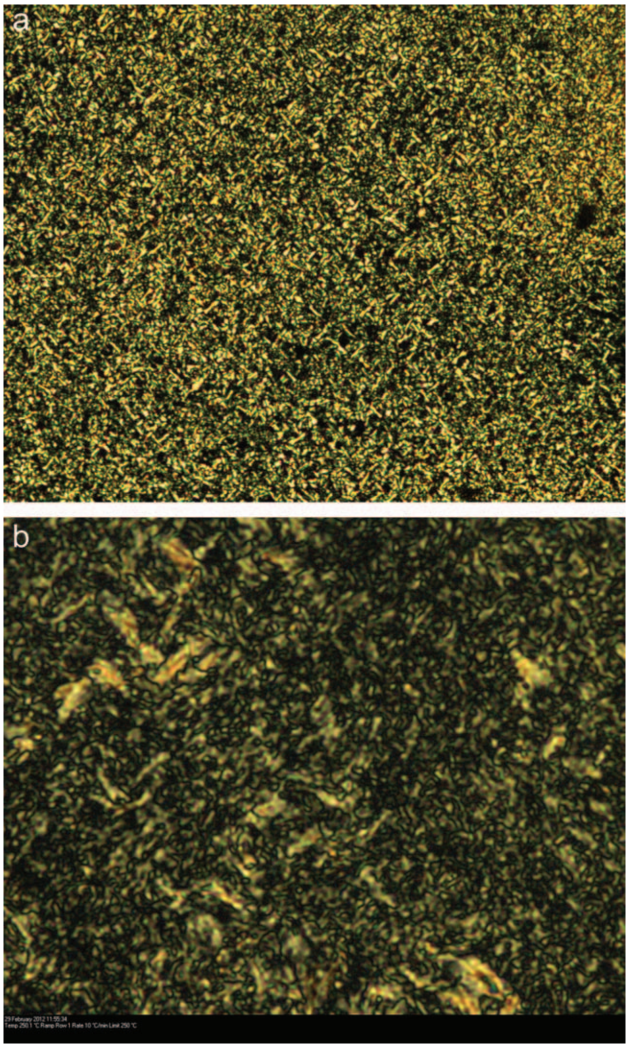


FIGURE 9 Optical microphotographs of poly(**BiBOX**-sebacic acid) at 30°C (a) and 250°C (b). Width of pictures is 400 μm; magnification of the objective is ×20.

endothermic signals. The isotropization temperatures decrease with the increasing length of the aliphatic chain in the backbone. The area between these two signals should represent a mesophase (approximately 250–300°C) as confirmed by microscopy measurements. Thermal properties of poly(**BiBOX**-succinic acid) and poly(**BiBOX**-adipic acid) are influenced by the fact that the signals of isotropization and degradation processes above 300°C are overlapped. Therefore, the signals of isotropization were missing in the records of second heating [Fig. 7(b)]. The overlapping of isotropization and degradation was confirmed in DSC measurements, where the temperature range of first heating was from 25 to 300°C.

The texture of crystalline and LC phases and phase transition temperatures of monomers and polymers were determined by a polarizing optical microscope equipped with a heating stage. Figure 8(a) shows a crystalline structure of the **BiBOX** below 250°C. This structure is stable up to 250°C and sublimation of the monomer starts at the temperature of 250°C. The sublimation is visible in the microscope as disappearing of the sample. The melting temperature of the **BiBOX** is 330°C and no LC phase was observed.

As follows from the observation under a polarizing microscope, melting temperature from the mesophase to an isotropic liquid is 260°C for the poly(**BiBOX**-dodecanedioic acid) [sample 5 in Fig. 7(a, b)] and 270°C for the poly(**BiBOX**-sebacic acid) [sample 4 in Fig. 7(a, b)], respectively. This is in accordance with DSC results [Fig. 7(a, b)]. The presence of the LC phase (probably nematic) was observed in AA+BB polymers at the isotropization temperatures. Figure 8(b) shows the melting of the mesophase of sample 5 at 260°C with nematic droplets in the back field indicating the isotropic phase. Figure 9 presents the microphotographs of the characteristic textures for poly(**BiBOX**-sebacic acid) (sample 4): (a) crystalline phase at 30°C and (b) nematic phase with the some crystalline parts (yellow rod-like spots).

CONCLUSIONS

Two different types of compounds containing a biphenyl unit, 2-oxazoline units and another functionality in the same molecule were synthesized. The first monomer of AB-type contained, beside the biphenyl as mesogen, a hydroxyl group and the 2-oxazoline, while the second type contains two 2-oxazoline groups and represents a monomer of the AA-type. Both monomers were used in thermally induced polyaddition reactions. The structure of all polymers was determined by NMR and IR spectroscopy. The rod-like structure of the biphenyl unit containing polymers influenced thermal properties and thermal stability. Thermal properties of AA+BB-type polymers are strongly influenced with the length of an alkyl linker. Microphotographs of polymers proved the existence of the mesophase with nematic texture in the related temperature range below the isotropization temperature.

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